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Ultraviolet Protection Characteristics of Silicone/Titanium Dioxide Composite Sheets

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Summary: Silicone/titanium dioxide (TiO_2) composite sheets were prepared from TiO_2 particles and silicone elastomer by a compression-molding process at 140 °C. The particles were produced through sol-gel method, and emulsion technique consecutively. The prepared composite sheets with thickness of 0.8 mm had ultraviolet radiation protection property such that the transmission of ultraviolet (UV) B ray through the sheets was less than 1%. The UVA ray transmitted the sheets in the range of 0.02–4% at 320 nm and 2–43% at 400 nm, depending on the amount of TiO_2 emulsion presented in the silicone elastomer. The composite sheets still remained transparent since the transmission of the visible light through the sheets was up to 60%. On the other hand, the transmissions of UVB ray, UVA ray, and visible light through the pure silicone elastomer sheets were in the range of 47–58%, 58–71%, and 71–88%, respectively. Comparable with silicone elastomer sheets, the addition of TiO_2 emulsion resulted in the composite sheets with higher strain and lower modulus; however, these differences in tensile properties were up to the amount of the emulsion in the silicone elastomer.

Keywords: composites; silicones; sol-gel; titanium dioxide (TiO_2); UV-vis spectroscopy

Introduction

Silicone elastomers have been widely used in many medical applications such as occlusive dressing due to their long term stability, biocompatibility, and high gas permeability. The silicone occlusive dressing has been investigated for use in the treatment of keloids and hypertrophic scars due to the capability to flatten and reduce the redness of scars.[1–2] Additionally, it is a non-invasive and effective treatment without any significant side effects. Scars are less resistant to ultraviolet radiation (UVR). Exposure of the scars, especially new scar, to UVR from sunlight can affect the treatment duration since UVR can increase the production of melanin resulting in the darkening of the scars. Silicone occlusive dressing is generally composed of a layer of silicone elastomer and a layer of silicone gel. Silicone is highly transparent resulting in high transmission of sun light to the skin surface. Hence, this study is aimed to develop a silicone elastomer sheet with anti-ultraviolet radiation property by incorporating TiO_2 particles (UV ray attenuator). TiO_2 in an emulsion form was incorporated in a silicone elastomer in order to maintain clarity of the silicone composite sheet.

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Experimental Part

Preparation of TiO_2 Emulsion

Tetrabutyl orthotitanate, acetylacetone, and water were mixed and stirred to obtain white or yellow transparent sol. The molar ratio of tetrabutyl orthotitanate, acetylacetone, and water at 1:1:1 and 1:2:1 was studied. The prepared sol was, then, mixed with palm oil at volume ratio of the sol to oil at 1:4 to obtain TiO_2 emulsion. Before adding into silicone, the TiO_2 emulsion was heated to about 160 °C until bubble gas disappeared.

Preparation of Silicone/TiO_2 Composite Sheet

The prepared TiO_2 emulsion was mixed with silicone elastomer base and curing agent (Dow corning MDX 4-4210) where the ratio of silicone elastomer base and curing agent is 10:1 by weight. The amount of TiO_2 emulsion was varied from 0.05–0.10% by weight of silicone elastomer base and curing agent. The mixture was stirred to obtain homogeneous sample, and degassed under vacuum in order to remove bubbles occurring in the mixing step. The mixture was, then, transferred to a stainless steel mold, and was compressed under temperature of 140 °C in order to obtain silicone/TiO_2 composite elastomer sheets with a thickness of 0.8 mm.

Characterization

Scanning Electron Microscopy

The fractured surface of the composite was observed using scanning electron microscope (SEM, model JSM-5410 (JEOL)). The fractured samples were surface coated with gold before investigation of their morphology.

Ultraviolet-Visible Light Transmission

UV-vis transmission spectra were recorded with the Perkin-Elmer® Lambda 900 spectrometer operating between 200 and 800 nm.

Tensile Testing

Tensile properties of the composite sheets were analyzed using a Universal Testing Machine (Instron model 55R4502). The specimens were cut to a dumbbell shape using die cut C according to ASTM D412. Tensile strength was measured following ASTM D412 (Test Method A) with the extension rate at ~500 mm/min. The reported tensile properties were based on the mean of five samples.

Results and Discussion

Figure 1 shows the presence of TiO_2 particles in the silicone composite sheet. TiO_2 in silicone elastomer was observed as bright particles. Size of TiO_2 particles are about 400–600 nm.

UV-vis transmission spectra of silicone and silicone/TiO_2 composite sheets were presented in Figure 2–3. The result shows that the amount and type of TiO_2 emulsion influenced the transmission capability of the composite sheets. As the TiO_2 content in the composite sheets was increased, UV-vis transmission of the composite sheets decreased. UVR transmission of composite sheets was much lower than that of pure silicone due to the UV absorption of TiO_2 particles. The transmission of UVB (280–315 nm) through the composite sheets was less than 1% at 280 nm. UVA (315–400 nm) transmission through the composite sheets was in the range of 0.02–4% at 320 nm and 2–43% at 400 nm. The transmission of visible light (400–760 nm) through pure silicone sheet was 88% at 760 nm, while that through the composite sheets was 20–62% and 63–80% for impregnation with emulsion prepared from tetrabutyl orthotitanate/acetylacetone/water at molar ratio of 1:1:1 and 1:2:1, respectively.

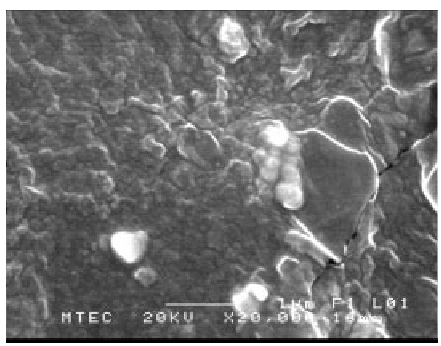

Figure 1.
Scanning electron micrograph of silicone/TiO_2 composite sheet

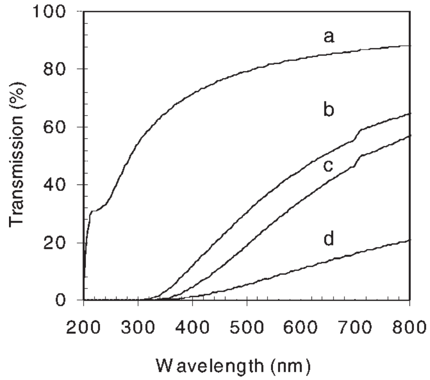

Figure 2.
UV-vis transmission spectra of (a) silicone elastomer; (b–d) silicone/TiO_2 composite elastomers with TiO_2 emulsion at quantity of 0.05, 0.08, and 0.10% by weight, respectively. The emulsion was prepared from mixing tetrabutyl orthotitanate, acetylacetone, and water at molar ratio of 1:1:1.

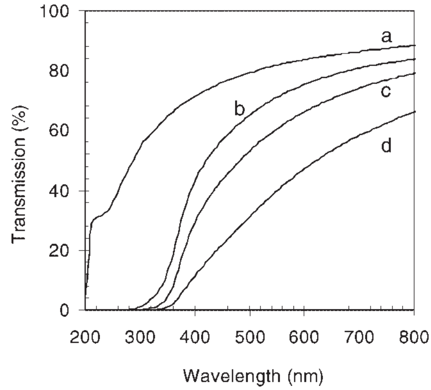

Figure 3.
UV-vis transmission spectra of (a) silicone elastomer; (b–d) silicone/TiO_2 composite elastomers with the TiO_2 emulsion at quantity of 0.05, 0.08, and 0.10% by weight, respectively. The emulsion was prepared from mixing tetrabutyl orthotitanate, acetylacetone, and water at molar ratio of 1:2:1.

The composite sheets prepared from the emulsion with the molar ratio of tetrabutyl orthotitanate, acetylacetone, and water at 1:1:1 showed more UV-vis absorption capability than those prepared at 1:2:1. The reason might be because the presence of higher concentration of acetylacetone (2 M in this study), functioning as an inhibitor for hydrolysis and condensation reactions of tetrabutyl orthotitanate, may lead to slower reaction process in forming TiO_2 particles. Thus, in this study, the addition of 1 molar of acetylacetone could help in the better formation of TiO_2 particles leading to better blocking UV-vis spectrum.

Tensile properties of silicone and silicone/TiO_2 composite elastomer sheets were presented in Table 1. The result shows that the presence of TiO_2 emulsion enhanced maximum strain, and reduced tensile strength and modulus. This can be the effect of the TiO_2 emulsion in silicone elastomer matrix where the presence of emulsion can soften the matrix leading to the reduction in modulus and the increase in strain.

Conclusions

Silicone/TiO_2 composite elastomer sheets showed property of UVR and visible light protection. UV transmission of the composite sheets was much less than that of pure silicone elastomer sheet. Comparing to

Table 1.
Tensile property of silicone and silicone/TiO_2 composite elastomer sheets at various percentage of TiO_2 emulsion addition. The ratios given in the parentheses are the molar ratio of tetrabutyl orthotitanate, acetylacetone, and water employed in the emulsion preparation step.

Samples	Max. Strain (%)	Tensile Strength (MPa)	Modulus (MPa)
Silicone	608 ± 30	8.80 ± 0.94	3.11 ± 0.20
Silicone/0.05%TiO_2 (1:2:1)	641 ± 23	8.20 ± 0.90	2.68 ± 0.29
Silicone/0.08%TiO_2 (1:2:1)	671 ± 28	7.52 ± 0.55	2.24 ± 0.10
Silicone/0.10%TiO_2 (1:2:1)	684 ± 61	8.55 ± 1.52	2.58 ± 0.29
Silicone/0.05%TiO_2 (1:1:1)	612 ± 39	8.32 ± 0.52	2.69 ± 0.15
Silicone/0.08%TiO_2 (1:1:1)	625 ± 65	7.16 ± 1.27	2.25 ± 0.26
Silicone/0.10%TiO_2 (1:1:1)	617 ± 28	6.94 ± 0.99	2.01 ± 0.19

tensile property of pure silicone elastomer, the composite sheets exhibited lower tensile strength and modulus. The prepared silicone/TiO_2 composite sheets can be used to fabricate silicone gel occlusive dressing with UVR protection property beneficial in scar treatment.

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